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<p>(54) Title: GAS PHASE DELIGNIFICATION OF LIGNOCELLULOSIC MATERIAL</p> <p>(57) Abstract</p> <p>A process for delignifying lignocellulosic material, such as wood pulp, which comprises treating the lignocellulosic material sequentially or simultaneously with gaseous <u>chlorine dioxide</u> and <u>ozone</u> which produces delignified cellulosic material and discharge effluents having reduced absorbed organic halides (AOX).</p> <p><i>Handwritten notes:</i></p> <p>(DZ) → E D → Z no wash) ↑ reducing agent p.19 DZE DZE DZE can repeat DZE reaction in mixers pumps fluffing pipe p.16 p.19 extraction 11/12/95</p>		

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GAS PHASE DELIGNIFICATION OF
LIGNOCELLULOSIC MATERIAL

The present invention relates to a process for sequential or simultaneous gas phase delignification of lignocellulosic material for use in paper making which produces delignified cellulosic material having reduced
5 absorbed organic halides (AOX).

Chlorine-based chemicals, such as chlorine, chlorine dioxide and hypochlorite have been used in pulp bleaching for several decades and continue to be used for removing lignin and bleaching the pulp to high
10 brightness. In general terms, the extent of delignification and bleaching (the degree of brightness obtained) is determined by the type of pulp being delignified and bleached and the proposed end use of the paper. In all instances, however, where chlorine-based
15 delignifying and bleaching agents have been employed in the prior art, there are produced chlorinated organics. These compounds are toxic and are present in the discharge effluents from one or more of the stages of the paper making process (eg. bleaching stage). A
20 relatively smaller percentage of such chlorinated organics remain in the pulp and eventually appear in the paper product.

In the past decade, there has been a growing concern about the environmental impact of the
25 chlorinated organic compounds present in paper and in discharge effluents. Undesirable chlorinated organics such as dioxin have been detected in the exhaust gases

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of incinerators burning municipal wastes including for example paper products made from chlorinated bleached pulps. Thus, it is desirable to limit the absorbed organic halides (AOX) discharged in the effluent per ton
5 of wood pulp to less than 2.0 kg.

Several options have been proposed or practiced to reduce or eliminate chlorinated organics in the bleaching process. The most straightforward method is to substitute non-chlorine bleaching chemicals such as
10 oxygen, peroxides, ozone, peracetic acid, etc. for chlorine-based bleaching chemicals. Oxygen delignification and bleaching is now a well-established commercial reality in pulp bleaching technology. Its use is restricted to partially remove lignin under alkaline
15 conditions - further bleaching must be done to remove the residual lignin color bearing groups. While whitening the pulp, great caution should be exercised to avoid the degradation of the carbohydrate fractions. When the complete removal of lignin is accomplished by
20 oxygen, the pulp strength suffers because of unacceptable destruction of the cellulose.

Hydrogen peroxide is widely used to reinforce the alkaline extraction stages which are carried out after the chlorination and chlorine dioxide stages, but so far
25 neither oxygen nor a combination of oxygen and hydrogen peroxide could match the efficiency of chlorination.

Ozone because of its high oxidation potential should offer a better alternative, but its uses are limited because it must be used in the gaseous state and
30 ozone generators produce only low concentrations of ozone in oxygen or air. Ozone has been used alone as a single stage bleaching agent, or in a multi-stage bleaching process which may include treatment with other bleaching agents such as oxygen, peroxides, chlorine

dioxide and hypochlorite. The fundamental bleaching variables affecting the use of ozone include (a) the type of pulp (hardwood or softwood), (b) the pulping process used to produce the pulp, (c) pre-treatment of the pulp prior to ozonization, (d) sequential treatment of ozone and other bleaching chemicals, (e) pulp consistency, (f) ozone concentration and charge, (g) temperature, (h) time, and (i) pH. But it was found that ozone, as a strong oxidant, tended to attack and degrade cellulose as is the case with oxygen. In the later instance, the degradation of cellulose is minimized by using a magnesium salt as a protector. However, it was determined that the amount of the ozone charge and the position of the ozone treatment in the bleaching process were important.

Another option to reduce the discharge of chlorinated organic compounds is to reduce the chlorine usage in the first stage of the bleaching process. Two alternatives that produce no significant degradation of pulp properties have been commercialized for this purpose. These are (a) extended delignification in the cooking stage and (b) oxygen delignification. These alternatives, with proper extraction, reduce the chlorinated organic compounds in the bleached pulp and ensuing effluent to sufficiently low levels.

A third option to reduce the generation of chlorinated organics in a bleaching process is to substitute chlorine dioxide for chlorine. Chlorine dioxide is a relatively strong oxidant compared to chlorine. To achieve the same degree of delignification, it requires only about thirty-eight weight percent chlorine dioxide on the pulp compared with one hundred weight percent of chlorine. However, these processes are of the DEDED type wherein the

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chlorine dioxide stage (D) is followed by the conventional extraction (E) and additional chlorine dioxide (D) stages. The pulp and discharge effluents resulting from the processes of this option contain
5 higher concentrations of chlorinated organics than are acceptable and/or desirable. Processes using both oxygen delignification and chlorine dioxide substitution have been suggested, but do not achieve the desired and/or regulated concentrations of chlorine containing
10 residues in either the pulp or the effluent.

Chlorine dioxide and ozone have found wide uses as disinfectants in water treatment/purification applications, delignifying and/or as a bleaching agent in pulp and paper production, and in a number of other
15 uses because of their high oxidizing power.

Ozone is used as a delignifying chemical to remove or reduce the lignin from the lignocellulosic material, but because of its high oxidizing power, it is indiscriminatory in its tendency to attack both lignin
20 and cellulose thereby producing inferior pulp.

Chlorine dioxide in solution has been used to brighten and produce a clean pulp in paper manufacture. However, it has generally been felt that the use of liquid chlorine dioxide in the first stage of a multiple
25 stage bleaching process is not as effective as is using chlorine as a delignifying agent. However, the use of elemental chlorine has the undesirable effect of producing organo-chlorine compounds, which are measurable as adsorbable organic halides (AOX), in the
30 effluent streams of processing facilities. Hence, as efforts have continued to focus on ways to eliminate or substantially reduce AOX discharge, chlorine dioxide has continued to be a popular agent in pulp processing, but as a brightening agent.

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There are a number of chlorine dioxide generator systems and processes available in the marketplace. Most of the very large scale generators utilize a chlorate salt, a chloride ion source or reducing agent, and a strong acid. In the presence of chloride ion and acid, chlorate ion reacts to produce a mixture of chlorine and chlorine dioxide. The chlorine present in these processes is an undesired by-product which adds to the AOX concentrations in discharge flow streams.

Many processes have been developed to produce chlorine dioxide with lower chlorine concentrations by adding a reducing agent. Some reducing agents which have been used in these applications include methanol or other organic compounds, sulfur, sulfur dioxide or other sulfur-oxygen species having a sulfur valence of less than +6, and carbon monoxide. When organic compounds are used, unreacted volatile organics, including organic acids, are present in the product gas. Using sulfur containing reducing agents, the sulfate or sulfuric acid produced accumulates as a waste product. When gaseous reducing agents, such as sulfur dioxide or carbon monoxide, are employed, reactor designs and process control systems must protect against unreacted reducing agent leaving the system with the chlorine dioxide gas.

Chlorine dioxide has been produced in prior art processes from chlorate salts by the addition of an excess of the acid used. While this acid is slowly neutralized by the accumulation of alkali metal ions that enter the process with the chlorate salt, the accumulation of salts must be removed as a waste stream. This waste stream is either liquid or solid in every process currently practiced commercially.

The preparation of chlorine dioxide from chloric acid has been accomplished to avoid the formation of an

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acidic alkali metal salt. Chloric acid is, however, not commercially available, although its preparation has been taught in U.S. Patent 3,810,969 issued May 14, 1974 to A.A. Schlumberger. Schlumberger teaches a process
5 for producing chloric acid by passing an aqueous solution containing from 0.2 gram mole to 11 gram moles per liter of an alkali metal chlorate such as sodium chlorate through a selected cationic exchange resin at a temperature from 5° to 40° C. The process produces an
10 aqueous solution containing from 0.2 gram mole to about 4.0 gram moles of HClO_3 per liter.

K.L. Hardee et al, in U.S. Patent No. 4,798,715 issued Jan. 17, 1989, describe a process to produce chlorine dioxide by electrolyzing a chloric acid
15 solution produced by passing an aqueous solution of an alkali metal chlorate through an ion exchange resin. The electrolysis is carried out using an electrocatalytic cathode where the catalyst is, for example, one or more valve metal oxides which may be
20 combined with a platinum group metal oxide, or a platinum group metal, or oxides of a platinum group metal, magnetite, ferrite, or mixed metal oxides.

The electrolyzed solution contains a mixture of chlorine dioxide and chloric acid, which is fed to an
25 extractor in which the chlorine dioxide is stripped off. The ion exchange resin is regenerated with hydrochloric acid and an acidic solution of an alkali metal chloride formed. Such processes require the regeneration of the ion exchange resin with acid to
30 remove the alkali metal ions and the use or treatment and disposal of the acidic salt solution. Also the concentration of chloric acid that can be produced by an ion exchange process is limited since more concentrated chloric acid solutions attack the ion exchange resins

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used in the process. Lastly, the production of chloric acid by means of a cation exchange resin is not economically attractive.

Commercial ozone generators produce ozone by a continuous high voltage electric discharge in presence of an oxygen containing feed gas. The ozone generator contains a stainless steel tube and a shell heat exchanger. High voltage alternating current is imposed on a high voltage electrode consisting of a permanent stainless steel tube on one side of a dielectric material. The dielectric glass tube centered in the stainless steel tube which has a ground electrode allows the electric discharge to occur as corona discharge across the discharge gap between the dielectric and the ground electrode. As the oxygen containing feed gas flows through the "corona", a portion of the oxygen is converted to ozone. Since much of the electrical energy supplied to form ozone is lost as heat, an efficient method of heat removal is incorporated into the design of the generator.

Gas phase bleaching with chlorine or chlorine dioxide has been proposed over the years in various patents and publications as a method of reducing the bleaching time while cutting chemical costs. Gas phase bleaching is carried out on higher consistency pulp using mixtures of chlorine dioxide and steam and/or inert gases such as air or nitrogen.

U.S. Patent No. 3,725,193, issued April 3, 1973 to R.M. DeMontigny et al., describes a process for bleaching high consistency pulps, which includes preheating the pulp by direct steaming. A gaseous mixture of chlorine dioxide diluted with steam or a non-reactive gas is then passed through the pulp. The contact period is in the order of a fraction of a

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second. The bleached pulp was then held in a retention vessel for 30 minutes. Unreacted chlorine dioxide was removed from a bleaching tower by aeration. The final pH of the bleached pulp was 5.2.

5 Ozone treatment of pulp is practiced under three pulp consistencies. They are ultra low consistency treatment, medium consistency treatment and high consistency treatment. High consistency treatment of pulp involves the use of gaseous ozone applications.

10 Advantages alleged for gas phase bleaching of high consistency wood pulps include superior control of bleaching because of the short retention times employed; reduced chemical usage for the same brightness; and low water usage and effluent volume. The gas phase
15 bleaching of pulp is well documented, but no information is available on the use of gaseous chlorine dioxide and ozone either sequentially or simultaneously for the delignification of pulps. Both chlorine dioxide and ozone are strong oxidizing agents, but their ability to
20 complement one another in the delignification process has been not explored.

 The lack of a process for generating chlorine dioxide gas instantaneously or by a process having inconsequential start-up and shut-down times has blocked
25 its successful use commercially of gas phase bleaching. A process has been found that produces chlorine dioxide gas which can be used directly from the generator without requiring the formation and storage of dilute aqueous solutions of chlorine dioxide which are
30 subsequently stripped or which do not have significant concentrations of elemental chlorine gas that damage the cellulose. After delignification there is substantially no residual chlorine dioxide requiring recovery or disposal. Also, unknown in the industry is the method

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of mixing the chlorine dioxide with another gas like ozone to get the powerful gaseous mixture having superior and selective oxidation ability to delignify pulp.

5 A recent process to reduce the AOX discharges from pulp mills has been disclosed by the Amcor Research and Technology Center in Australia which uses an oxygen pretreatment step to passivate the pulp and enhance the reactivity of liquid chlorine dioxide applied in a first
10 stage delignification operation, followed immediately by an alkaline extraction stage without an intermediate washing step. This process substantially reduces the AOX discharge, but still requires the pretreatment step. There exists the need for a simplified process to
15 directly delignify lignocellulosic material.

 Canadian patents number 2,032,315; 2,031,848; and 2,031,850 teach the sequential addition of aqueous chlorine dioxide and ozone at points separated from one another and each being at at least one place in the line
20 and this stage being free from intermediate washing between places for addition. Heterogenous sequential treatment of pulp with aqueous solutions of ozone and chlorine dioxide require repeated filtering and thickening of pulp stock to adjust for the various
25 consistency requirements of each treatment step.

 These problems are solved in the process of the present invention by using gaseous chlorine dioxide and ozone sequentially or simultaneously to delignify and bleach pulp and thereby reduce the adsorbed organic
30 halides (AOX) in the delignified and bleached pulp and discharge effluents. A further reduction of AOX is obtained by conducting a direct alkaline extraction without intermediate washing stage after the bleaching step.

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It is an object of the present invention to provide an improved process for delignifying lignocellulosic material.

Another object of the present invention is to mix
5 the chlorine dioxide gas from the state of the art generation processes with an ozone oxygen gas mixture to get a highly reactive chlorine dioxide and ozone gas mixture.

It is another object of the present invention to
10 provide a first stage treatment with a gaseous mixture of chlorine dioxide and ozone which dramatically reduces the AOX discharges.

Another feature of the present invention is that any residual elemental chlorine formed in the chlorine
15 dioxide generation is oxidized by mixing and reacting it with ozone, thereby eliminating the chances of chlorine to react with pulp to generate AOX.

Another object of the present invention is that any residual elemental chlorine formed in the reaction
20 between chlorine dioxide and lignocellulosic material is destroyed by the reaction of lignocellulosic material with ozone, thereby reducing the chances for the formation of absorbable organic halides (AOX).

Another object of the present invention is that
25 gaseous chlorine dioxide added to the lignocellulosic material acts as an acidic pH buffer of pH 2 - 5, the pH range conducive for ozone delignification.

Yet another object of the invention is that chlorine dioxide addition to the pulp inhibits the
30 carbohydrate degradation reactions of ozone which are responsible for the strength loss of the pulp.

It is an advantage of the present invention that lower AOX concentrations are achieved with pulps having higher pH values.

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It is still another advantage of the present invention that a clean pulp material is obtained in less time and at lower cost in needed equipment when compared with conventional processes.

5 These and other objects, features and advantages are obtained by an improved process for delignifying lignocellulosic material which comprises treating the lignocellulosic material sequentially or simultaneously with gaseous chlorine dioxide and ozone and then
10 transporting it into a reaction chamber where it is retained for a short period of time to complete the reaction and delignification of the lignocellulosic material. Then an alkaline extraction is performed. The delignified material is then separated from the
15 effluent. This effluent contains less than about 1.0 kg absorbable organic halides (AOX) per ton of lignocellulosic material.

Suitable pulps which can be bleached include any of those which are commonly used such as chemical kraft,
20 sulfite or mechanical and recycle pulps. Pulp having any suitable consistencies may be delignified including those of about 15 percent or higher, for example, from about 25 to about 60 percent can be treated by the process of the present invention. The pulps are
25 preferably shredded or fluffed.

Chlorine dioxide gas used as a reactant in the process of the present invention preferably contains low concentrations of elemental chlorine and preferably small amounts of inert gases, such as nitrogen or air.
30 Suitable chlorine dioxide gas used in delignification of pulp is a mixture of chlorine dioxide, gaseous oxygen, and water vapor. Partial pressure of chlorine dioxide in the gas stream is between 10 to 100 mm of Hg. The chlorine dioxide gas has a low elemental chlorine

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*chlorine
free*

content of less than about 18 percent. The chlorine dioxide gas can also be substantially free of chlorine, preferably less than about 2 percent by weight, and more preferably less than about 1.5 percent by weight based

5 on the weight of chlorine dioxide in the gas. The gaseous mixture contains varying concentrations of oxygen and water vapor. The amount of oxygen can be independently varied to provide molar ratios of O_2 to ClO_2 by volume of from about 1:4 to about 50:1. Water
10 vapor or steam is preferably the primary diluent in the gaseous mixture and replaces other inert gases which are normally used. As a diluent, steam supplies heat to the pulp and minimizes cooling by evaporation which occurs when, for example, air is used as the diluent.

15 Gaseous mixtures containing chlorine dioxide suitable for use in the novel process of the present invention preferably can be produced from concentrated solutions of chloric acid.

Conversion of the chloric acid to chlorine
20 dioxide can be accomplished, for example, by cathodic reduction in an electrolytic cell or by contacting the chloric acid with a suitable catalyst in the presence of heat. In an alternative process, highly acidic aqueous solutions containing chlorate ions, including chloric
25 acid, perchlorate ions and hydrogen ions are reacted to produce a gaseous mixture of chlorine dioxide, oxygen and water vapor (steam). The gaseous mixture has low concentrations of inert gases, such as air or nitrogen, and yet provides reduced risks to spontaneous explosions
30 or "puffs". The aqueous solutions have an acid concentration of at least 2 molar, preferably at least 3 molar, and a concentration of chlorate ions of at least 0.02 molar and preferably from about 0.1 to about 3 molar. These acidic solutions preferably are

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substantially free of ionic impurities such as chloride ions, alkali metal and alkaline earth metal ions.

The hydrogen ion concentration from acid in the aqueous solutions may be provided by non-oxidizable
5 inorganic acids such as sulfuric acid, phosphoric acid, chloric acid or perchloric acid. Preferably, the acidic solutions are reacted in the presence of a catalyst which promotes oxygen evolution.

Suitable as oxygen-evolving catalysts are, for
10 example, metals and oxides of the elements of Group VIIIA of the Periodic Table of Elements. Thus metals such as the platinum group metals including platinum, palladium, iridium, rhodium or ruthenium; and mixtures or alloys of these platinum group metals may be
15 employed. Additionally oxides of platinum group metals such as iridium, rhodium or ruthenium, as well as mixtures of these oxides with platinum group metals or alloys of these precious metals could be suitably employed. Likewise, iron alloys such as stainless
20 steel, nickel or nickel based alloys, and cobalt based alloys can be used as oxygen-evolving catalysts in the process of the invention. Other oxygen-evolving catalysts include semiconductive ceramics known as perovskites. To suppress or minimize the auto-oxidation
25 of chloric acid to perchloric acid, for example where an oxygen-evolving catalyst is employed, it is preferred to use, as the source of chlorate ions, a mixture of chloric acid and a non-oxidizable inorganic acid in which the concentration of chloric acid is low, for
30 example, less than about 20 percent by weight of the aqueous solution providing chlorate ions. These processes for generating chlorine dioxide can be started up in a few minutes and similarly stopped in a short

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time so that storage of ClO_2 gas or dissolution in water or a solvent is not required.

High purity concentrated chloric acid solutions are produced by the oxidation of high purity hypochlorous acid solutions. One process suitable for producing the chloric acid solutions heats a hypochlorous acid solution, containing from about 35 to about 60 percent by weight of HOCl , at a temperature in the range of from about 25 to about 120° C. Another process for producing the high purity chloric acid solution utilizes anodic oxidation of the high purity concentrated hypochlorous acid solution in an electrolytic cell having an anode compartment, a cathode compartment, and a cation exchange membrane separating the anode compartment from the cathode compartment.

In operation, this process includes feeding an aqueous solution of hypochlorous acid to the anode compartment, and electrolyzing the aqueous solution of hypochlorous solution at a temperature of from about 0° to about 40°C. to produce the chloric acid solution.

Chloric acid solutions can be produced by these processes in any concentrations desired up to about 45% by weight of HClO_3 . However, preferred concentrations are those in the range of from about 30 to about 40% by weight of HClO_3 .

Generation of the chlorine dioxide gas from the reaction mixture containing chloric acid and the non-oxidizable inorganic acid is preferably conducted at atmospheric pressure in the presence of a diluent gas, such as oxygen, nitrogen or air. The temperature of the reactor mixture should not exceed 120°C, more preferably not more than about 90°C, to avoid decomposition of the chlorine dioxide in the gas phase. Where subatmospheric pressures are utilized, for example, pressures can be in

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the range of from about 15 to about 750, preferably from about 100 to about 500, and more preferably from about 150 to about 300 mm of Hg. At these pressures the temperature of the reaction mixture is in the range of
5 from about 40°C to about 90°C, and preferably from about 50°C to about 80°C. The temperatures and pressures for subatmospheric pressures are selected to maintain continuous boiling of the reaction mixture.

The chlorine dioxide gas generator must be in
10 water balance to operate in steady state conditions. The rate of heat addition to the generator determines the quantity of water that is evaporated to maintain steady state concentration, it is necessary to evaporate water continuously at about the same rate at which water
15 is added, with the chloric acid feed solution adjusted for water formed by reaction of the chloric acid.

Alternately, chlorine dioxide gas can be obtained from any commercially available generators directly producing gaseous chlorine, or by removing the gas prior
20 to going to an adsorber for liquifaction, such as those available from Albright and Wilson Americas under the model names R-8, R-9 and R-10, or from other suppliers of similar commercial equipment.

Ozone gas can be obtained from any commercially
25 available generators producing ozone by direct electric discharge through air or oxygen. The concentration of ozone from the reactor should be not less than 6 percent by weight on the oxygen feed, but not limited to or not exceeding 13 percent by weight of oxygen feed, the point
30 of self detonation of ozone. Preferable concentrations are from about 6 to 8 percent. The ozone gas from the reactor may be taken to a mixing chamber where it may be used to mix the chlorine dioxide gas from the novel generation process described above. Chlorine dioxide

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can also be obtained from state of the art generators such as the R-8 generator or from other generators supplied by similar commercial equipment vendors.

The process of the invention can be practiced
5 using any suitable prior art apparatus such as a conventional bleaching tower.

Delignification of pulp may be affected in the initial stages of a multi-stage bleaching process, as well as in any D or DZ stages. The process of the
10 invention requires a rapid mixing and short retention in an apparatus similar to the existing first stage equipment capable of mixing a mixture of gaseous chlorine dioxide and ozone with lignocellulosic material. The delignification of unbleached
15 lignocellulosic material or pulp is accomplished with the use of a gaseous mixture of chlorine dioxide and ozone produced by one of the aforementioned processes and simultaneously charging the gaseous mixture to the pulp or sequentially charging the individual gases to
20 the pulp. The gaseous chlorine dioxide has low concentrations, or is substantially free, of elemental chlorine and is combined with a direct alkaline extraction step in the absence of an intermediate washing to reduce the AOX concentrations in the
25 discharge stream. The delignification of unbleached lignocellulosic material or pulp may be carried out in any suitable equipment in which the unbleached pulp can be contacted with the chlorine dioxide gas. For practical reasons any reactor should be gas tight.
30 Suitable gas tight equipment includes, for example, agitated mixers, static mixers, ribbon blenders, steam chests, high consistency shear mixers, MC pumps, MC mixers, high velocity pipe lines, fluffers, etc.

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Pressure requirements for the feed of the gaseous mixture of chlorine dioxide and ozone to ensure stability are critical, especially if the gaseous mixture is being introduced into a vacuum chamber. For example, partial pressure of the chlorine dioxide in the chlorine dioxide gas must be limited to about 100 mm of Hg to insure stability. If the chlorine dioxide is generated under a vacuum in the generator, it must be maintained under a vacuum to ensure introduction into the reaction chamber.

The pulp material should be in the range of about 20 to about 50 percent consistency, and more preferably about 30 percent consistency. The pulp material can spend from about 5 seconds to about 45 minutes in the reaction chamber, preferably from about 5 seconds to about 5 minutes, and more preferably from about 5 seconds to about 1 minute contact time in the reaction chamber before exiting.

The feed rate of the chlorine dioxide and ozone gas mixture to the lignocellulosic material or pulp can be controlled so that it can be passed through at least one time, and possibly as many as two or three times, such as by the use of pressure differential between the upper inlet side and the lower outlet side before the gas exits through the reaction chamber for reclamation.

The lignocellulosic material or pulp can then be passed directly to an alkaline extractor apparatus to undergo the alkaline treatment. Although it is preferred that the alkaline extraction occur without any intermediate washing in the process of the instant invention, it is possible to use an intermediate wash prior to an alkaline treatment.

The elemental chlorine-free ClO_2 and ozone mixture is admixed with the pulp in the reactor which is

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at any suitable pressure including atmospheric, subatmospheric or superatmospheric pressures. In a preferred embodiment, the reactor is at subatmospheric pressures which are preferably slightly below those employed in the chlorine dioxide or ozone generator. 5 Optionally at superatmospheric pressures an eductor can be used which employs ozone and oxygen gas mixture to dilute and to remove chlorine dioxide from the generator and supply it to the pulp reactor. The chlorine dioxide 10 and ozone gas mixture is used in amounts which provide a concentration or ratio of gas mixture to pulp that is suitable for delignifying the unbleached chemical pulp to the desired degree, as indicated, for example, by the selected Kappa number as determined by TAPPI test method 15 T236 cm-85 and accepted by the industry.

The delignification of the pulp using the process of the invention is accomplished in surprisingly short contact times, with the delignification rate being independent of pulp temperatures. The temperature of 20 the delignification reaction is not critical and delignification can be carried out at surprisingly low temperatures, from about ambient temperature. Temperatures in the range of from about ambient to about 90°C, preferably ambient to about 80°C, and more 25 preferably, from about 20°C to about 60°C can be employed. At these temperatures minimal time is required.

To maximize the efficiency of the gaseous mixture of chlorine dioxide and ozone, delignification of the 30 pulp normally is carried out under acidic conditions and the acidity can be derived from the chlorine dioxide gas. For example, in any delignification stage following a caustic extraction stage, the pH of the pulp to be treated normally is adjusted so that the final pH

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of the delignified pulp before extraction is in the range from about 1 to about 6. Residual chlorine dioxide and ozone gas mixture can be suitably removed, such as by passing an inert gas through the pulp and the gaseous mixture can then be passed through a catalytic converter to reclaim oxygen which can be sent to the chlorine dioxide generator or to the ozone generator or to both for further use..

An extraction stage (E) is then carried out without an intervening washing step with, for example, caustic soda to solubilize the higher molecular weight oxidized lignins, to hydrolyze organic chlorides to salts, etc. Where chlorine dioxide has not been removed prior to extracting, a suitable reducing agent can be added with or prior to adding the extracting agents, such as sodium thiosulfate, sodium hydrosulfite, sodium sulfide, sodium sulfite, hydrogen peroxide, or combinations thereof.

The extraction is conducted at temperatures of 60° to about 90°C., and a residence time of about 60 minutes where the final pH is 10.5 or higher. The extraction stage may include the addition of oxygen, a peroxide such as hydrogen peroxide, or hypochlorite, or a combination thereof for enhanced performance. The extracted pulp is filtered and washed to remove water soluble lignins and low molecular weight organic chlorides, among others.

After the initial delignification and extraction using the process of the present invention, the delignified chemical pulp has a Kappa number in the range of from about 1 to about 10, and preferably from about 2 to about 8.

The extracted pulp may be subsequently further delignified, for example, using the process of the

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invention or any known bleaching stage to achieve the final brightness desired.

It has been discovered that the novel process of the present invention reduces the formation of toxic by-products organic halides. These undesirable by-products, collectively identified as adsorbable organic halides (AOX), require effluents from pulp bleaching processes to undergo expensive treatment methods to eliminate AOX prior to discharge to sewers.

The effluent discharge from the bleaching process of the present invention has less than about 2.0 kg adsorbable organic halides (AOX) per ton of wood pulp. AOX, as the term is used herein refers to the sum of the AOX, i.e. adsorbed organic halides, of the several stages of bleaching and alkaline extraction with or without washing. The pulp produced by the present invention has a brightness and viscosity that meet or exceed the requirements of industrial papermaking.

To further illustrate the invention the following examples are provided without any intention of being limited thereby. All parts and percentages are by weight unless otherwise specified and temperatures are in degrees Celsius.

EXAMPLE 1

SIMULTANEOUS ADDITION OF GASEOUS MIXTURE CHLORINE DIOXIDE AND OZONE

To a jacketed reaction vessel containing a gas distribution plate is added 100 grams of oven dried fluffed softwood pulp having a consistency of 35%. The initial Kappa No. of the softwood pulp is 30.0, but not certainly confined to the Kappa number mentioned. The

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temperature of the pulp is maintained between 25°C to 65°C. The pulp reaction vessel is connected to two gas scrubbers, each of which contains a 10% solution of potassium iodide. The chlorine dioxide generator is initially filled with about 1500 grams of perchloric acid containing about 40 percent by weight of HClO_4 , the perchloric acid contains about 15 grams of ruthenium dioxide, RuO_2 . A gaseous mixture of chlorine dioxide, oxygen and water vapor is generated by feeding a chloric acid solution containing about 37.16 percent by weight of HClO_3 . During chlorine dioxide generation, the generator is maintained at a temperature between about 70° and 73°C by regulating the feed rate of the chloric acid, and by providing sufficient heat of reaction to evaporate the water present in the chloric acid solution and that formed during the generation of chlorine dioxide. The ozone reactor is a commercial reactor using oxygen as the feed gas for ozone generation. The ozone generator is maintained at temperatures between 10° and 25°C. Two separate gas lines, independently carrying ozone and chlorine dioxide from the respective generators are connected to a small mixing chamber prior to entering the bottom of the reaction vessel. Then the gaseous mixture is distributed into the pulp through a perforated sparger. The softwood pulp is treated for a time between 1 - 5 minutes with the gaseous mixture. Each delignified pulp sample is equally divided, one half to be washed and the other not washed prior to extraction (E). Where washing is employed the filtrate and the wash water are collected. Extraction of the delignified pulp is carried out by adding the indicated amount of about 3.5% NaOH by weight on pulp of a 10 percent sodium hydroxide solution. The operating consistency of pulp is about 10 percent. The pulp is

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held at about 70°C. for about 60 minutes. The extracted pulp is dried, washed and the Kappa Number is determined to be less than 10. The absorbable organic halides (AOX) in the combined solution mixture of the bleach
5 filtrate, wash water, extraction liquor and wash water is determined to be less than 1.0 kg/metric ton of pulp.

EXAMPLE 2

SEQUENTIAL ADDITION OF GASEOUS CHLORINE DIOXIDE AND OZONE

10 A continuously stirred hot water jacketed reaction vessel containing a gas distribution device is loaded with 100 gm of oven dried shredded and fluffed softwood pulp having a consistency of about 35 percent. The reaction vessel can act as an equipment vessel for
15 rapid mixing of gas with pulp as well as a retention vessel for the continuation of the delignifying process after mixing the gases with the pulp. The initial Kappa number of the pulp is about 30.0. The initial pulp temperature is at ambient conditions, but warmed up to
20 about 80°C and preferentially maintained between about 40°C and about 60°C.

The outlet of the reactor is connected to a series of potassium iodide traps containing 10 percent KI which are acting as gas scrubbers for both the
25 chlorine dioxide and ozone exiting the reaction vessel. Between the reaction vessel and the gas scrubbers, the catalytic convertor is employed to remove the organics carried over by the exiting gases and also to remove the moisture from the oxygen which was the carrier gas for
30 both chlorine dioxide and ozone. Two separate gas lines, independently carrying ozone and chlorine dioxide

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from the respective generators are connected to the bottom of the reaction vessel and distributed into the pulp through a perforated sparger. Each line has a gas metering device to measure accurately the gas flow to the reactor. The chlorine dioxide gas line is also using a spectrophotometric device to measure the concentration of chlorine dioxide flowing to the reactor. The ozone supply line has a concentration measurement and monitoring unit utilizing UV spectrophotometry to measure the concentration of ozone in the carrier gas. A feedback control unit is used to adjust the oxygen feed to the ozone generator.

The gases can be fed sequentially either by charging ozone first and then chlorine dioxide and vice versa. In the event of chlorine dioxide being fed first to react with pulp, the initial pulp pH has a range from 2 to about 8. On the other hand, if ozone is the gas first to react with the pulp, then the pH of the pulp is adjusted by using an acid, preferably sulfuric acid. The pH of the pulp ranges from 2 to 5, but preferably less than 3. Also in case of chlorine dioxide being charged first to the pulp, the exit gas is taken directly to the KI traps by-passing the catalytic convertor. The chlorine dioxide feed to the pulp is calculated on the basis of the Kappa factor, a measure of chemical charge determined by the Kappa number of the pulp. The Kappa factor is in the range of 0.5 to 2.0. The time for the reaction is varied from one minute to five minutes, but preferably less than about 2 minutes. The ozone charge on the pulp is varied from 0.1 percent to 2.0 percent. The reaction time is varied from one minute to five minutes, but preferably less than about two minutes. The reaction can be carried out in subatmospheric, atmospheric, or superatmospheric

2-7 D
D → Z

pressure. The pressure range is 10 mm of Hg to 760 mm Hg to 1520 mm Hg, preferably between 100 to 1520 mmHg.

Each delignified pulp sample is equally divided, one half to be washed and the other not washed prior to
5 extraction (E). Where washing is employed, the filtrate and the wash water are collected. Extraction of the delignified pulp is carried out by adding the indicated amount of about 3.5 percent sodium hydroxide by weight on pulp of a 10 percent sodium hydroxide solution. The
10 operating consistency of pulp is about 10 percent. The pulp is held at about 70°C for about 60 minutes. The extracted pulp is dried, washed and the Kappa number is determined to be less than 10. The adsorbed organic halides (AOX) in the combined solution mixture of the
15 bleach filtrate, wash water, extraction liquor and wash water is determined to be less than 1.0 kg/metric ton of pulp.

The pulp from the extraction step is treated with one or more bleaching sequences involving chlorine
20 dioxide in aqueous or gaseous form, alkaline extraction with sodium hydroxide reinforced by oxygen and/or hydrogen peroxide and a gaseous mixture of chlorine dioxide and ozone and combinations thereof to obtain pulp of required brightness and strength. The adsorbed
25 organic halides (AOX) in the later bleach plant effluent from the bleaching sequences are found to be less than 0.3. kg/metric ton of pulp.

While the invention has been described above with references to specific embodiments thereof, it is
30 apparent that many changes, modifications and variations in the materials, arrangements of parts and steps can be made without departing from the inventive concept disclosed herein. Accordingly, the spirit and broad

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scope of the appended claims is intended to embrace all such changes, modifications and variations that may occur to one of skill in the art upon a reading of the disclosure.

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WHAT IS CLAIMED IS:

1. A process for delignification of lignocellulosic material characterized by contacting lignocellulosic material sequentially or simultaneously with a gaseous
5 mixture of chlorine dioxide and ozone.

2. The process of claim 1 characterized in that the acidity during delignification is controlled such that the delignified material will have a pH ranging from about 2 to about 5.

10 3. The process of claim 1 characterized in that the treatment with said gaseous mixture is effected at subatmospheric pressure.

4. The process of claim 1 characterized in that said process is carried out at a temperature ranging
15 from about 50° C to about 80° C.

5. The process of claim 1 characterized in that the gaseous chlorine dioxide contains from 0 to about 20 percent by weight of chlorine.

6. The process of claim 5 characterized in that
20 the chlorine dioxide is produced by admixing an aqueous solution of chloric acid containing at least about 30 percent by weight of HClO_3 with a non-oxidizable inorganic acid.

7. The process of claim 1 characterized in that
25 said lignocellulosic material is wood pulp.

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8. The process of claim 7 characterized in that said wood pulp has a consistency from about 20 to about 50 percent.

9. The process of claim 1 characterized in that the
5 delignified material is subjected to alkaline extraction with an alkali metal hydroxide directly following the delignification step.

10. The process of claim 1 characterized in that the delignification is effected at a pressure selected
10 from the group consisting of subatmospheric, atmospheric, and superatmospheric.

11. The process of claim 10 characterized in that the temperature is from about 50°C to about 80°C.

12. The process of claim 11 characterized in that
15 said lignocellulosic material is wood pulp having a consistency of at least about 15 percent.

13. The process of claim 12 characterized in that said chlorine dioxide is produced by admixing chloric acid containing at least 30 percent by weight of HClO_3
20 with an inorganic acid selected from the group consisting of sulfuric acid, phosphoric acid and perchloric acid.

14. The process of claim 13 characterized in that the delignified pulp is subjected to alkaline extraction
25 with an alkali metal hydroxide directly following the delignification step.

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15. The process of claim 1 characterized in that the process is carried out simultaneously using a mixture of gaseous chlorine dioxide and ozone.

16. The process of claim 15 characterized in that
5 said lignocellulosic material is wood pulp having a consistency of at least 15 percent.

17. The process of claim 15 characterized in that said chlorine dioxide is produced by admixing chloric acid containing at least 30 percent by weight of HClO_3
10 with an inorganic acid selected from the group consisting of sulfuric acid, phosphoric acid and perchloric acid.

18. The process of claim 15 characterized in that the delignified pulp is subjected to alkaline extraction
15 with an alkali metal hydroxide directly following the delignification step.

19. The process of claim 1 characterized in that the delignified material is subjected to a subsequent bleaching step which comprises treating the
20 lignocellulosic material sequentially or simultaneously with gaseous chlorine dioxide and ozone.

20. The process of claim 1 characterized in that the sequential treatment of the lignocellulosic material is first with gaseous chlorine dioxide and then with
25 ozone.

21. The process of claim 1 characterized in that the sequential treatment of the lignocellulosic material is first with ozone and then gaseous chlorine dioxide.

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22. The process of claim 1 characterized in that the gases are fed to a continuously stirred reactor vessel through a concentration measurement means and a metering means.

- 5 23. The process of claim 1 characterized in that the continuously stirred reactor vessel is used as a rapid mixing means and/or a retention means to continue and complete the delignification of the lignocellulosic material.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/00408

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :D21C 9/14; D21C 9/153

US CL :162/65,67,88,89

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/65, 67, 88, 89

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	US,A, 4,959,124 (Tsai) 25 September 1990. See column 5, lines 8-10, column 5, lines 6-7, table 2.	1,2,4,5,7, <u>9-11,20,21</u> 1-23
Y	US,A, 5,034,095 (Kido et al) 23 July 1991. See entire document.	3
Y	US,A, 3,810,969 (Schlumberger) 14 May 1974 See column 2, lines 22-40.	13,14,6,17
Y	US,A, 3,725,193 (Montigny et al) 03 April 1973 See entire document.	8,12-14,16
Y	US,A, 4,902,381 (Meredith) 20 February 1990. See column 3, lines 29-31.	15,18,22,23

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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24 FEBRUARY 1993

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/00408

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Summary of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US A, 1,957,937 (Campbell et al) 08 May 1934. See page 2, lines 127-141.	15,18,16,17